MIL-53(AL) AND GRAPHENE OXIDE NANOCOMPOSITES FOR DYE ADSORPTION

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Abstract

Textile manufacturers produce large amounts of wastewater every year as a result of global demand. Waste dyes are highly resilient against physical processes, insoluble in water, and resistant to detergents. Carcinogenic and mutagenic effects are linked to these dyes, making them a large health hazard. Current dye removal methods are highly complex and inefficient. Thus, a new means of removing textile dyes from wastewater is needed. Nanomaterials are one such possibility, since they exhibit traits unique from bulk materials. One key trait is their surface area to volume ratio. Since the materials are so small, they're almost able to be considered two dimensional in certain instances. A high surface area is closely linked to adsorption potential, making nanomaterials a promising candidate for dye removal. This project has two portions: material synthesis and adsorption testing. Material synthesis sets up the adsorption testing phase by fabricating enough nanomaterials for testing. The nanomaterials used for this project are MIL-53 (Al) and graphene oxide (GO). MIL-53 (Al) and GO were chosen since they exhibit good stability in water and effective geometrical structures for water filtration. Synthesized composites of the two materials varying in mass of GO will be tested as well. Adsorption testing uses slightly acidic (pH 5.6) methyl blue and methyl orange solutions of varying parts per million (PPM) concentrations. The tests examine effects of initial concentration, duration of exposure, and temperature effects on adsorption potential. Nanomaterials reached equilibrium adsorption after 12 hours of mixing. Most materials efficiently removed up to 90% or greater of dye particles in solutions with initial concentrations of 100 PPM for both dye colors. Increased temperatures reduced adsorption potential of nearly all materials tested for both dye colors.

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1. Introduction

700,000 tons of wastewater are produced annually by the textile industry [1, 2, 3]. Dyeing agents pose a unique challenge when trying to manage and treat wastewater. They are specifically designed to resist various cleaners and bleaches found in household laundry detergents. They can resist light degradation and do not break down easily in the presence of water [4].

The increase in world population compounds environmental challenges caused by industrial innovations. One such challenge is the contamination of water sources by wastewater from textile manufacturers. While some waste comes in the form of solid materials such as fabric, the most significant pollutants found are industrial dyes. Textile manufacturers use these dyes across the world in order to provide for the high demand for clothing.

There are a variety of textile dyes used throughout the industry, but the most used are azo dyes. Azo dyes make up 65% of industrial colorants thanks to their ease and low cost of fabrication [5, 6]. However, due to their molecular composition and shape, azo dyes are linked with negative environmental and health effects [6]. Multiple studies link azo dyes with mutagenic and carcinogenic effects [7, 8]. In addition to the substantial health risks, textile waste impacts marine plant growth. As mentioned before, azo dyes are resistant to light degradation. Thus, azo dyes released into the ocean prevents sunlight from reaching algae and other plant life and inhibits photosynthesis.

Due to their size and molecular structure, nanomaterials are an optimal candidate for removing azo dyes from wastewater. Nanomaterials are classified as being 10^{-9} meters in diameter. At such a small scale, the individual structures form nearly two-dimensional sheets. This is a large advantage in adsorption, since certain properties depend on a surface area to

volume [9]. The two nanomaterials chosen for this project were graphene oxide (GO) and MIL-53 (Al) metal organic framework (MOF). GO is variant of sheet graphene with oxygen groups along the surface. Thanks to its shape, GO only permits pure water to pass through its intermolecular openings, making it a promising candidate for water treatment. "MOFs, a newly emerged class of nanoporous materials that are organic-inorganic hybrids constructed from metal ion nodes linked by organic linkers to form a three-dimensional crystal lattice structure, have received considerable attention due to their ultra-high surface areas, low densities, diverse topologies, and tunable pore sizes," [10]. Based on these properties, MOFs are also highly useful for water treatment applications. Specific to this project, MIL-53 (Al) was selected thanks to its stability in water [11], unlike many other MOFs which are very instable in the presence of moisture. This study utilized varying mass-ratio composites of MIL-53 (Al) and GO to find an optimal ratio for different dyes. Research was also done on varying dye coloration, exposure duration, initial dye concentration, and thermodynamic effects on adsorption potential.

2. Materials and Methods

2.1 Synthesis of GO

GO was prepared using Hummer's method. 0.5 grams of sodium nitrate, 0.5 grams of graphite powder, and 23 milliliters of 99% sulfuric acid were added in a one-liter beaker and stirred for four hours. Three grams of potassium permanganate were added to the mixture. The beaker should remain in the ice bath during this step to prevent overheating of the solution. Once solution temperature has stabilized, the beaker is removed from the ice bath and the temperature is increased to 35°C and stirring continues for one hour. 46 mL of deionized water is then added to the mixture. This rapidly increases the solution's temperature, requiring a very slow, controlled addition of the deionized water. The solution is stirred at a constant 95°C for two

hours. The solution risks the possibility of boiling at temperatures in excess of 98°C, rendering the product useless. The solution is removed from the heating source and allowed to cool to room temperature (approximately 23°C). 100 mL of deionized water stirred into the solution for half an hour before 10 mL of 30% hydrogen peroxide is added. After another 30-minute stirring cycle, the solution is triple washed and centrifuged at 8000 RPM for 10 minutes with deionized water. After the washing is complete, the remaining mixture is freeze dried for two days.

2.2 Synthesis of MIL-53 (Al)

MIL-53 (Al) was synthesized using 0.788 grams of aluminum nitrate nonahydrate, 0.518 grams of terephthalic acid, and 30 milliliters of dimethylformamide. The components were mixed until an even consistency was achieved. The mixture was placed in a steel autoclave with a Teflon inset. The autoclave was then placed in a vacuum oven for three days at a temperature of 130°C. The autoclave and inset were removed at the end of this duration. The resulting white gel was centrifuged at a setting of 8000 RPM for 10 minutes, and triple washed using methanol. The resulting mixture was placed in a 100°C oven for 24 hours. The white product was immersed in 30 milliliters of methanol for one day before being triple washed using the same process as before. The final material was vacuum dried at 110°C overnight.

2.3 Synthesis of MIL-53 (Al) – GO Composites

Composites are classified by their mass percentage of GO. They are synthesized using the same method as MIL-53 (Al), however a set amount of GO is added during the initial phase of mixing before being placed in the vacuum oven for 72 hours at 130°C. The composites synthesized used 0.039 grams of GO for 3% MIL-53 (Al)-GO, 0.065 grams for 5%, and 0.13 grams for 10%.

2.4 Characterization

All materials were examined using a Rigaku MiniFlex II x-ray diffractometer, courtesy of the UAF geology department. X-ray diffraction allows one to verify the success of the synthesis process. All materials exhibited peaks within a two-degree range of acceptable values.

2.5 Solution Synthesis

Solutions of methyl blue and methyl orange simulated textile dyes for this study. Dye solutions varied in concentration measured in parts per million (ppm). The study used multiple dyes to see if the solution's charge would affect adsorption potential. The samples prepared ranged from 40 to 200 ppm for concentration and kinetic tests and 1.25 to 20 ppm to generate calibration curves.

2.6 Adsorption Measurements

2.6.1 Calibration Curves

Calibration curves were generated using six 100 mL samples of methyl blue and orange solution with concentrations of 1.25, 2.5, 5, 10, and 20 ppm. The samples were prepared by diluting 100 ppm bulk solution to the desired concentration. All samples' pH was then adjusted to 5.6 using 0.1M hydrochloric acid and sodium hydroxide. Samples were then placed in a UV-Vis spectrometer three times to obtain an average value for blue and orange dye solutions. After calibration was complete, kinetic and concentration tests could commence.

2.6.2 Kinetics Testing

Kinetics testing determined the effect of exposure duration on adsorption potential. Samples with set concentrations, volumes, and pH (200 ppm, 50 mL, 5.6 pH) were used for the kinetic testing. 20 mg of nanomaterials were added to the dye solution before being placed on a VWR S-500 orbital shaker at 175 rpm. Individual samples were then removed after the following shaking durations: five minutes, 10 minutes, 15 minutes, 30 minutes, 40 minutes, one hour, three

hours, five hours, eight hours, 10 hours, and 12 hours. Samples were then centrifuged at 9700 rpm for half an hour. The centrifuged samples were run through a UV-Vis spectrometer three times. The average value of the tests presented achieved equilibrium concentration (C_e) at the various time steps. The results were then analyzed to determine the point in time where adsorption reached an equilibrium point. Equilibrium adsorption capacity (q_e) was determined with Equation (1):

$$q_e = \frac{C_0 - C_e}{M} V \quad (1)$$

where q_e is in units of mg of adsorbent per gram of solid dye particles, C_0 is initial concentration in mg solid dye particle/L deionized water, C_e is the equilibrium concentration also in mg solid dye particle/L deionized water, M is mass of adsorbent in mg, and V is volume of dye solution in mL. The time step where adsorption reached equilibrium would then be used as a standard for later testing durations. A new set of concentration testing was then used to measure maximum adsorption potential.

2.6.3 Concentration Testing

Concentration testing measured the effect of initial dye solution concentration on adsorption potential. Testing procedures used samples diluted from stock 200 ppm solution. Sample concentrations used were 40, 60, 80, 100, 150, and 200 ppm. The pH was adjusted to 5.6 using 0.1M HCl and NaOH before adding 20 mg of nanomaterial adsorbents. Samples were then placed on a shaker table with a speed setting of seven for 12 hours. They were then centrifuged for 30 minutes at 9700 rpm. The centrifuged samples were then analyzed with an UV-Vis spectrometer. The average adsorption from three measurements of each sample was recorded and is seen below. These results were used to determine multiple traits of each adsorbent from

Langmuir and Freundlich isothermal models. A final set of tests was performed to analyze if thermodynamics played any part in adsorption.

2.6.4 Thermodynamic Response

Thermodynamic testing followed the same procedures as concentration and kinetics testing. Thermodynamic testing, however, made use of an Eppendorf New Brunswick Excella E24 Incubated Orbital Shaker at a setting of 125 rpm due to stability constraints instead of the 175 rpm used with the VWR S-500 orbital shaker at room temperatures. Heated concentration and kinetic testing were performed at room temperature, 35°C, and 45°C.

Results from these various tests were then tabulated and analyzed using Langmuir and Freundlich isotherm models. "The Langmuir model assumes a surface with homogeneous binding sites, equivalent adsorption energy, and no interaction between adsorbed species," [12]. From this model, one can determine maximum adsorption capacity, q_{max} (mg adsorbent/g solid dye particle), equilibrium concentration, C_e (mg adsorbent/L dye solution), and equilibrium adsorption capacity, q_e, which shares the same units as q_{max}. One also calculates the Langmuir constant, K_L (L/mg), which shows how easily the adsorbent will naturally bond to the adsorbate. These values are found with Equation (2) [13]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \tag{2}$$

Another Langmuir model value that is used is the separation factor, R_L, which measures how well the adsorbent can be described with the Langmuir isotherm model. R_L is calculated with the equation below [13]:

$$R_L = \frac{1}{1+K_L C_0} \tag{3}$$

where C_0 is the initial concentration of dye solution in mg of dye particles per liter of deionized water and K_L is the Langmuir constant. A separation factor greater than one shows that the

adsorbent is unlikely to be a Langmuir isotherm. Factors between zero and one are likely Langmuir isotherms. A factor equal to one implies a linear isotherm. A factor of zero implies irreversibility.

Freundlich models, unlike Langmuir, assume the adsorbents active sites have differing energies and that the adsorption surface is heterogeneous. Properties related to this model are determined with the following equation [13]:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (4)$$

K_F [(mg/g)·(L/mg)$^{1/n}$] is the adsorption capacity. $1/n$ is the adsorption intensity. These constants are unique to Freundlich isotherm models.

Another factor that is calculated and considered from concentration testing results is changes in Gibbs free energy (ΔG^0, [kJ/mol]). Gibbs free energy change tells how spontaneously adsorption occurs. ΔG^0 is calculated using the equation below [14]:

$$\Delta G^0 = -RTlnK_0 \quad (5)$$

where R is the universal gas constant (8.314 J/mol·K), T is temperature in Kelvin, and K_0 is the thermodynamics equilibrium constant derived from the intersection of the linear plot of $ln(q_e/C_e)$ vs. q_e. After finding ΔG^0, entropy (ΔS^0) and enthalpy (ΔH^0) are found from Van't Hoff plots. The equation relating the three parameters is listed below [14]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

3. Results and Discussion

3.1 Characterization

Characterization tests determined the accuracy with which nanomaterials were synthesized. Materials were characterized by x-ray diffraction and compared with published results. Materials that fell within a ±2° range of published angles were considered viable for

adsorption. All nanomaterials used in this project fell within the acceptable range of published values [13].

3.2 Kinetics Testing

Kinetics testing results are displayed below in Table 1.

Table 1: Kinetics testing results of various nanomaterials at multiple temperatures.

Adsorbent	Dye Color	Temperature (K)	Time (min)	C0 (mg/L)	Ce (mg/L)	V/M (mL/mg)	Qe (mg/g)	% Adsorption
3% MIL-53(Al)-GO	Orange	298	5	200	138.51	2.5	153.73	30.75
			10		115.75		210.63	42.13
			15		128.54		178.66	35.73
			20		110.90		222.75	44.55
			30		105.12		237.21	47.44
			40		96.34		259.16	51.83
			60		92.56		268.60	53.72
			180		87.60		280.99	56.20
			300		75.78		310.54	62.11
			480		75.92		310.20	62.04
			600		83.03		292.42	58.48
			720		77.86		305.35	61.07
		308	5		91.47		271.33	54.27
			10		87.26		281.85	56.37
			15		92.57		268.57	53.71
			20		99.17		252.07	50.41
			30		98.57		253.59	50.72
			40		97.58		256.05	51.21
			60		88.25		279.37	55.87
			180		83.53		291.18	58.24
			300		84.16		289.61	57.92
			480		71.75		320.62	64.12
			600		98.45		253.87	50.77
			720		90.32		274.21	54.84
		318	5		105.16		237.10	47.42
			10		108.57		228.59	45.72
			15		105.56		236.10	47.22
			20		99.29		251.79	50.36
			30		94.47		263.82	52.76
			40		95.84		260.40	52.08
			60		82.37		294.07	58.81
			180		80.03		299.92	59.98
			300		84.50		288.74	57.75

			480		76.12		309.70	61.94
			600		65.91		335.23	67.05
			720		69.97		325.08	65.02
	Blue	298	5		124.59		188.54	37.71
			10		113.71		215.74	43.15
			15		105.67		235.81	47.16
			20		105.36		236.60	47.32
			30		97.30		256.74	51.35
			40		102.76		243.09	48.62
			60		93.06		267.35	53.47
			180		86.49		283.77	56.75
			300		77.91		305.21	61.04
			480		84.36		289.10	57.82
			600		88.13		279.67	55.93
			720		79.88		300.29	60.06
		308	5		128.74		178.15	35.63
			10		127.29		181.77	36.35
			15		106.19		234.51	46.90
			20		104.77		238.09	47.62
			30		104.07		239.83	47.97
			40		107.00		232.50	46.50
			60		119.03		202.43	40.49
			180		103.29		241.78	48.36
			300		101.03		247.41	49.48
			480		92.52		268.70	53.74
			600		70.88		322.80	64.56
			720		88.62		278.44	55.69
		318	5		115.71		210.73	42.15
			10		97.80		255.50	51.10
			15		115.71		210.73	42.15
			20		100.77		248.06	49.61
			30		105.93		235.16	47.03
			40		104.44		238.91	47.78
			60		94.57		263.58	52.72
			180		92.60		268.50	53.70
			300		81.52		296.19	59.24
			480		87.89		280.27	56.05
			600		88.58		278.54	55.71
			720		87.98		280.05	56.01
Adsorbent	Dye Color	Temperature (K)	Time (min)	C0 (mg/L)	Ce (mg/L)	V/M (mL/mg)	Qe (mg/g)	% Adsorption

5% MIL-53(Al)-GO	Orange	298	5	200	153.54	2.5	116.15	23.23
			10		160.97		97.58	19.52
			15		161.38		96.55	19.31
			20		154.27		114.34	22.87
			30		149.22		126.96	25.39
			40		149.74		125.66	25.13
			60		145.87		135.34	27.07
			180		137.27		156.82	31.36
			300		142.56		143.60	28.72
			480		136.71		158.23	31.65
			600		130.46		173.86	34.77
			720		138.94		152.64	30.53
		308	5		154.23		114.42	22.88
			10		148.92		127.71	25.54
			15		153.96		115.09	23.02
			20		144.15		139.63	27.93
			30		142.04		144.89	28.98
			40		140.84		147.90	29.58
			60		125.75		185.62	37.12
			180		122.44		193.91	38.78
			300		120.41		198.97	39.79
			480		121.68		195.81	39.16
			600		129.16		177.10	35.42
			720		116.51		208.73	41.75
		318	5		134.28		164.29	32.86
			10		131.88		170.31	34.06
			15		134.37		164.06	32.81
			20		130.10		174.74	34.95
			30		142.44		143.91	28.78
			40		129.55		176.11	35.22
			60		129.32		176.71	35.34
			180		101.65		245.88	49.18
			300		105.86		235.35	47.07
			480		113.87		215.33	43.07
			600		98.45		253.87	50.77
			720		96.10		259.74	51.95
	Blue	298	5		135.58		161.05	32.21
			10		101.09		247.28	49.46
			15		142.76		143.09	28.62
			20		111.14		222.16	44.43
			30		120.74		198.16	39.63
			40		101.36		246.61	49.32
			60		110.17		224.59	44.92

			180		77.10		307.25	61.45
			300		69.86		325.34	65.07
			480		85.66		285.84	57.17
			600		84.60		288.50	57.70
			720		92.53		268.69	53.74
		308	5		104.23		239.43	47.89
			10		127.26		181.86	36.37
			15		129.44		176.41	35.28
			20		138.21		154.47	30.89
			30		113.25		216.88	43.38
			40		104.70		238.24	47.65
			60		131.29		171.78	34.36
			180		69.02		327.44	65.49
			300		92.72		268.21	53.64
			480		82.36		294.11	58.82
			600		77.94		305.15	61.03
			720		83.14		292.16	58.43
		318	5		104.42		238.94	47.79
			10		101.13		247.17	49.43
			15		95.70		260.74	52.15
			20		108.42		228.94	45.79
			30		83.55		291.12	58.22
			40		96.62		258.45	51.69
			60		100.93		247.67	49.53
			180		83.28		291.80	58.36
			300		88.30		279.24	55.85
			480		51.47		371.34	74.27
			600		71.69		320.76	64.15
			720		72.61		318.47	63.69
Adsorbent	Dye Color	Temperature (K)	Time (min)	C0 (mg/L)	Ce (mg/L)	V/M (mL/mg)	Qe (mg/g)	% Adsorption
10% MIL-53(Al)-GO	Orange	298	5	200	156.90	2.5	107.75	21.55
			10		186.90		32.76	6.55
			15		167.81		80.48	16.10
			20		144.90		137.74	27.55
			30		135.93		160.19	32.04
			40		123.96		190.10	38.02
			60		130.62		173.46	34.69
			180		126.88		182.79	36.56
			300		115.34		211.66	42.33
			480		108.66		228.35	45.67

			600		117.62		205.95	41.19
			720		103.66		240.85	48.17
		308	5		294.12		-235.30	-47.06
			10		245.26		-113.15	-22.63
			15		417.09		-542.73	-108.55
			20		178.65		53.37	10.67
			30		165.45		86.38	17.28
			40		276.78		-191.94	-38.39
			60		306.03		-265.08	-53.02
			180		242.51		-106.27	-21.25
			300		269.83		-174.59	-34.92
			480		200.29		-0.71	-0.14
			600		185.05		37.37	7.47
			720		152.99		117.52	23.50
		318	5		126.02		184.95	36.99
			10		125.92		185.20	37.04
			15		129.23		176.93	35.39
			20		128.13		179.68	35.94
			30		123.92		190.19	38.04
			40		114.60		213.49	42.70
			60		121.52		196.21	39.24
			180		112.84		217.91	43.58
			300		87.96		280.09	56.02
			480		95.21		261.98	52.40
			600		96.78		258.04	51.61
			720		97.80		255.50	51.10
	Blue	298	5		131.25		171.88	34.38
			10		103.23		241.93	48.39
			15		99.41		251.46	50.29
			20		104.91		237.73	47.55
			30		108.29		229.29	45.86
			40		102.67		243.31	48.66
			60		97.15		257.12	51.42
			180		75.01		312.48	62.50
			300		93.60		266.00	53.20
			480		93.70		265.75	53.15
			600		94.29		264.28	52.86
			720		85.21		286.97	57.39
		308	5		99.04		252.40	50.48
			10		94.75		263.12	52.62
			15		82.80		293.00	58.60
			20		76.89		307.78	61.56
			30		90.86		272.85	54.57

			40		79.88		300.31	60.06
			60		79.68		300.79	60.16
			180		63.62		340.94	68.19
			300		67.91		330.23	66.05
			480		77.96		305.11	61.02
			600		38.92		402.71	80.54
			720		62.92		342.71	68.54
		318	5		105.07		237.32	47.46
			10		105.95		235.13	47.03
			15		107.43		231.42	46.28
			20		114.18		214.54	42.91
			30		92.29		269.27	53.85
			40		107.34		231.64	46.33
			60		92.57		268.58	53.72
			180		62.55		343.62	68.72
			300		64.32		339.20	67.84
			480		67.05		332.36	66.47
			600		85.54		286.15	57.23
			720		64.97		337.57	67.51
Adsorbent	Dye Color	Temperature (K)	Time (min)	C0 (mg/L)	Ce (mg/L)	V/M (mL/mg)	Qe (mg/g)	% Adsorption
MIL-53(Al)	Orange	298	5	200	143.30	2.5	141.74	28.35
			10		127.96		180.09	36.02
			15		132.11		169.72	33.94
			20		121.04		197.41	39.48
			30		124.39		189.03	37.81
			40		98.54		253.66	50.73
			60		110.49		223.78	44.76
			180		101.61		245.98	49.20
			300		86.36		284.09	56.82
			480		101.99		245.01	49.00
			600		85.20		286.99	57.40
			720		94.11		264.71	52.94
		308	5		148.54		128.64	25.73
			10		142.40		143.99	28.80
			15		144.61		138.48	27.70
			20		139.26		151.85	30.37
			30		114.25		214.37	42.87
			40		132.15		169.61	33.92
			60		124.36		189.11	37.82
			180		90.14		274.65	54.93

			300		82.31		294.23	58.85
			480		85.95		285.13	57.03
			600		101.17		247.07	49.41
			720		103.57		241.07	48.21
		318	5		116.26		209.36	41.87
			10		118.38		204.05	40.81
			15		110.12		224.69	44.94
			20		114.24		214.41	42.88
			30		104.48		238.79	47.76
			40		101.70		245.74	49.15
			60		104.76		238.11	47.62
			180		110.53		223.67	44.73
			300		124.81		187.98	37.60
			480		86.31		284.22	56.84
			600		127.51		181.22	36.24
			720		72.90		317.75	63.55
	Blue	298	5		149.95		125.13	25.03
			10		146.79		133.03	26.61
			15		134.78		163.04	32.61
			20		133.83		165.44	33.09
			30		133.67		165.81	33.16
			40		134.17		164.58	32.92
			60		128.26		179.36	35.87
			180		111.83		220.42	44.08
			300		108.89		227.78	45.56
			480		104.51		238.73	47.75
			600		98.62		253.45	50.69
			720		103.39		241.54	48.31
		308	5		130.50		173.76	34.75
			10		115.75		210.63	42.13
			15		130.29		174.27	34.85
			20		126.83		182.93	36.59
			30		120.93		197.68	39.54
			40		125.00		187.49	37.50
			60		127.10		182.25	36.45
			180		79.08		302.29	60.46
			300		85.99		285.02	57.00
			480		90.76		273.09	54.62
			600		61.50		346.25	69.25
			720		74.29		314.29	62.86
		318	5		164.41		88.98	17.80
			10		163.55		91.11	18.22
			15		133.15		167.13	33.43

			20		144.82		137.95	27.59
			30		125.17		187.08	37.42
			40		146.20		134.49	26.90
			60		118.63		203.42	40.68
			180		139.85		150.37	30.07
			300		93.90		265.25	53.05
			480		103.82		240.44	48.09
			600		89.20		277.01	55.40
			720		89.74		275.64	55.13
Adsorbent	Dye Color	Temperature (K)	Time (min)	C0 (mg/L)	Ce (mg/L)	V/M (mL/mg)	Qe (mg/g)	% Adsorption
GO	Orange	298	5	200	166.28	2.5	84.30	16.86
			10		144.69		138.28	27.66
			15		126.50		183.75	36.75
			20		138.86		152.86	30.57
			30		156.27		109.33	21.87
			40		139.79		150.52	30.10
			60		147.63		130.92	26.18
			180		141.47		146.31	29.26
			300		145.86		135.36	27.07
			480		136.00		160.00	32.00
			600		125.51		186.21	37.24
			720		126.43		183.92	36.78
		308	5		156.43		108.92	21.78
			10		166.64		83.40	16.68
			15		185.97		35.08	7.02
			20		177.19		57.02	11.40
			30		187.28		31.81	6.36
			40		182.58		43.54	8.71
			60		174.87		62.82	12.56
			180		187.64		30.89	6.18
			300		165.36		86.61	17.32
			480		185.61		35.97	7.19
			600		178.95		52.62	10.52
			720		174.46		63.85	12.77
		318	5		156.50		108.76	21.75
			10		144.94		137.66	27.53
			15		151.56		121.10	24.22
			20		161.13		97.17	19.43
			30		142.85		142.87	28.57
			40		140.49		148.78	29.76

			60		148.03		129.93	25.99
			180		151.08		122.29	24.46
			300		147.51		131.22	26.24
			480		177.74		55.65	11.13
			600		185.72		35.71	7.14
			720		187.10		32.24	6.45
	Blue	298	5		121.38		196.55	39.31
			10		119.02		202.46	40.49
			15		106.95		232.63	46.53
			20		105.50		236.26	47.25
			30		100.26		249.36	49.87
			40		85.39		286.52	57.30
			60		71.92		320.20	64.04
			180		44.24		389.40	77.88
			300		36.81		407.97	81.59
			480		15.91		460.22	92.04
			600		17.38		456.56	91.31
			720		17.45		456.37	91.27
		308	5		49.18		377.04	75.41
			10		45.79		385.53	77.11
			15		38.03		404.91	80.98
			20		60.95		347.63	69.53
			30		31.44		421.41	84.28
			40		50.95		372.63	74.53
			60		49.51		376.22	75.24
			180		9.71		475.74	95.15
			300		0.00		500.00	100.00
			480		0.00		500.00	100.00
			600		0.00		500.00	100.00
			720		0.00		500.00	100.00
		318	5		103.14		242.15	48.43
			10		107.28		231.80	46.36
			15		103.14		242.15	48.43
			20		94.29		264.28	52.86
			30		65.28		336.81	67.36
			40		91.22		271.95	54.39
			60		13.82		465.46	93.09
			180		33.51		416.24	83.25
			300		12.76		468.09	93.62
			480		26.83		432.93	86.59
			600		24.69		438.28	87.66
			720		19.16		452.10	90.42

As mentioned before, kinetics testing showed the exposure time at which adsorbents reached total saturation. This time to reach saturation would then be employed in later concentration tests. Most materials reached peak adsorption between three to five hours of exposure; however, some took longer to achieve equilibrium. Thus, it was decided the full 12-hour mixing duration should be utilized since all materials reached equilibrium during that time period.

3.3 Adsorption Isotherms

Concentration testing examined initial dye concentration effects on adsorbents' maximum capacity. The goal of these tests was to determine the initial concentration that would fully saturate various adsorbents. The other objective of concentration testing was to examine various adsorption isotherm properties using Langmuir and Freundlich models at multiple temperatures. Concentration testing also measured changes in Gibbs energy. Tables 2, 3, and 4 detail these various measured and calculated parameters.

Table 2: Langmuir Isotherm parameters

Adsorbent	Temperature (K)	Dye Color	Langmuir			
			q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
3% MIL-53(Al)-GO	298	Orange	400.00	0.01	0.77	0.65
	308		294.12	0.00	0.92	1.00
	318		285.71	0.01	0.89	1.00
	298	Blue	277.78	0.01	0.96	0.99
	308		250.00	0.00	0.99	1.00
	318		263.16	0.00	0.99	1.00
5% MIL-53(Al)-GO	298	Orange	294.12	0.01	0.88	0.99
	308		277.78	0.16	0.24	0.90
	318		277.78	0.00	0.95	1.00
	298	Blue	370.37	0.00	0.98	0.96
	308		344.83	0.00	0.98	0.94
	318		303.03	0.00	1.00	1.00
10% MIL-53(Al)-GO	298	Orange	232.56	0.00	0.94	1.00
	308		263.16	0.00	0.93	1.00
	318		212.77	0.00	0.97	1.00
	298	Blue	357.14	0.00	0.99	0.95
	308		322.58	0.01	0.97	0.93
	318		333.33	0.00	1.00	1.00
MIL-53(Al)	298	Orange	158.73	0.01	0.86	1.00

	308		270.27	0.02	0.70	0.79
	318		312.50	0.01	0.82	0.99
	298		232.56	0.01	0.94	0.79
	308	Blue	243.90	0.02	0.91	0.94
	318		250.00	0.00	1.00	1.00
	298		250.00	0.12	0.29	0.26
	308	Orange	312.50	0.15	0.26	0.29
GO	318		222.22	0.11	0.32	0.37
	298		370.37	0.00	1.00	1.00
	308	Blue	370.37	0.00	1.00	1.00
	318		370.37	0.00	1.00	1.00

Table 3: Freundlich Isotherm Parameters

Adsorbent	Temperature (K)	Dye Color	Freundlich		
			1/n	K_F (mg/g)·(L/mg) (1/n)	R^2
	298		0.3564	103.3271326	0.5254
	308	Orange	0.2316	137.6755734	0.7877
3% MIL-53(Al)-GO	318		0.2368	128.4705892	0.6592
	298		0.0632	171.9493574	0.7068
	308	Blue	0.0689	180.0617774	0.9118
	318		0.0734	186.9609927	0.9162
	298		0.2399	124.5117389	0.8854
	308	Orange	0.1866	119.7372789	0.4793
5% MIL-53(Al)-GO	318		0.1926	151.7447753	0.632
	298		0.0838	204.5270008	0.6892
	308	Blue	0.0737	205.4699922	0.5549
	318		0.0898	222.738848	0.9155
	298		0.1887	128.1498138	0.7302
	308	Orange	0.1522	151.305353	0.9884
10% MIL-53(Al)-GO	318		0.1481	137.4279803	0.5086
	298		0.0874	221.4064162	0.6564
	308	Blue	0.0679	199.6767881	0.5112
	318		0.0968	230.2809304	0.9291
	298		0.0761	116.0823671	0.2032
	308	Orange	0.2288	100.624926	0.5484
MIL-53(Al)	318		0.3201	100.3736778	0.9576
	298	Blue	0.1052	133.4063855	0.6545
	308		0.0497	153.5613252	0.5688

	318		0.0711	193.4656544	0.9807
GO	298	Orange	0.6581	13.80043343	0.4281
	308		0.6193	15.30531265	0.6061
	318		0.6343	14.70371231	0.4219
	298	Blue	0.0903	328.422208	0.732
	308		0.0848	361.296879	0.5271
	318		0.0866	367.3811996	0.528

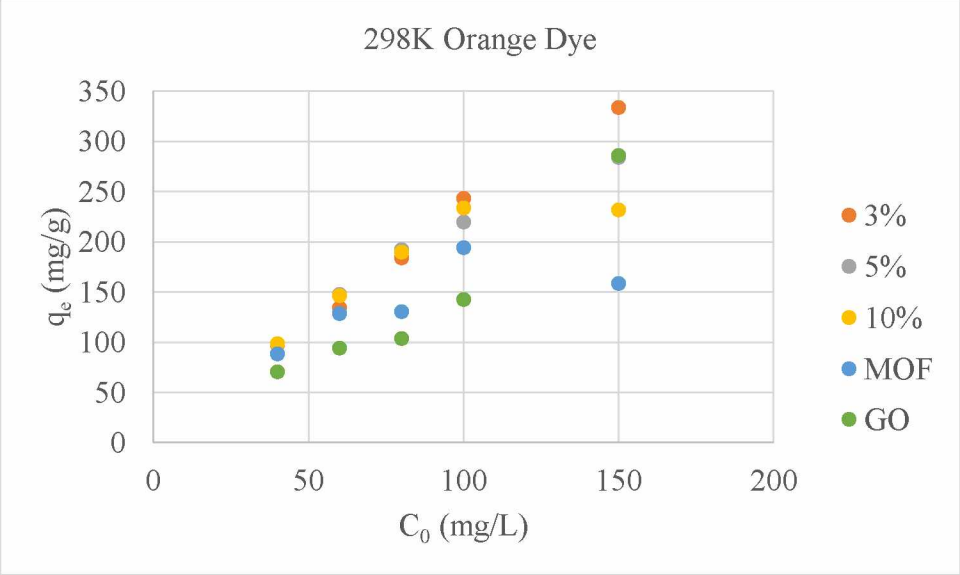
Table 4: Gibbs Free Energy Change Properties

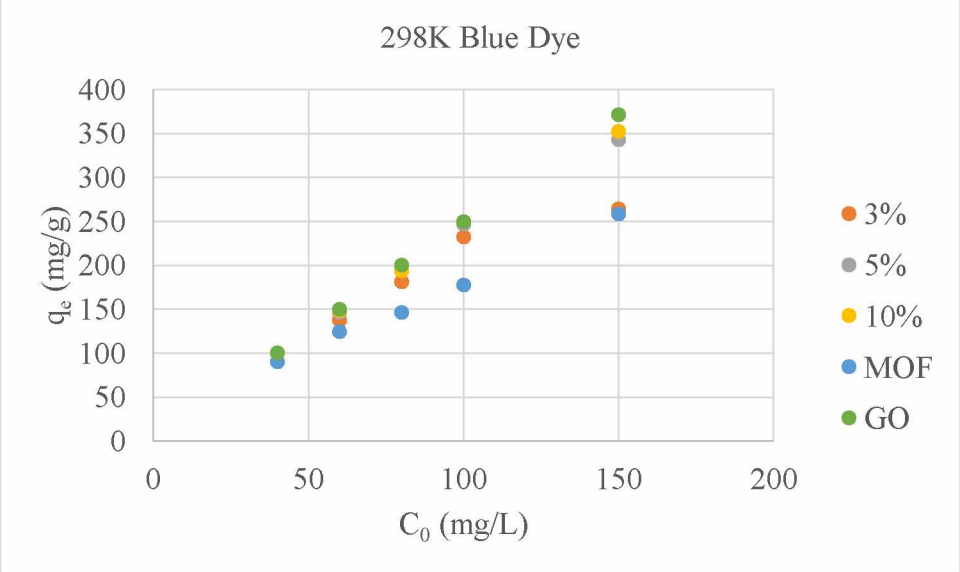
Adsorbent	Dye Color	Gibbs					
		T (K)	K_0	ΔH^0 (kJ/mol)	ΔS^0 (J/K)	ΔG^0 (kJ/mol)	R^2
3% MIL-53(Al)-GO	Orange	298	12.761	13557	58.192	-6308.87	0.5778
		308	6.8861			-4940.91	
		318	5.8303			-4661.29	
	Blue	298	15.139	6987.4	46.367	-6732.24	0.8826
		308	18.625			-7488.81	
		318	18.122			-7659.57	
5% MIL-53(Al)-GO	Orange	298	6.788	2413.2	22.913	-4744.94	0.1383
		308	4.7383			-3983.64	
		318	7.1566			-5203.19	
	Blue	298	12.761	11490	59.296	-6308.87	0.8764
		308	12.739			-6516.16	
		318	17.027			-7494.79	
10% MIL-53(Al)-GO	Orange	298	6.9637	-3050.9	7.1316	-4808.25	0.0124
		308	10.345			-5983.11	
		318	6.5052			-4950.88	
	Blue	298	12.903	8247.7	48.581	-6336.29	0.8733
		308	12.667			-6501.65	
		318	15.865			-7307.91	
MIL-53(Al)	Orange	298	4.149	11804	51.044	-3525.26	0.8612
		308	4.2098			-3680.81	
		318	5.5818			-4546.13	
	Blue	298	8.2751	36049	138.74	-5235.73	0.9947
		308	14.225			-6798.69	
		318	20.694			-8010.46	
GO	Orange	298	1.0808	-695.28	-1.1023	-192.511	0.0013

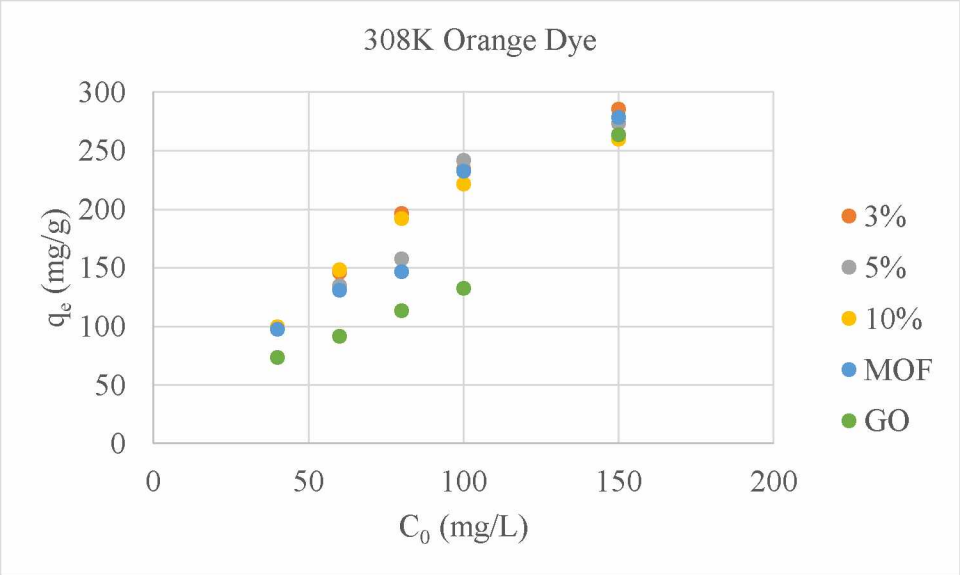
		308	1.3166			-704.331	
		318	1.0666			-170.465	
	Blue	298	18.722	295.77	25.377	-7258.54	0.9969
		308	18.977			-7536.76	
		318	18.867			-7766.09	

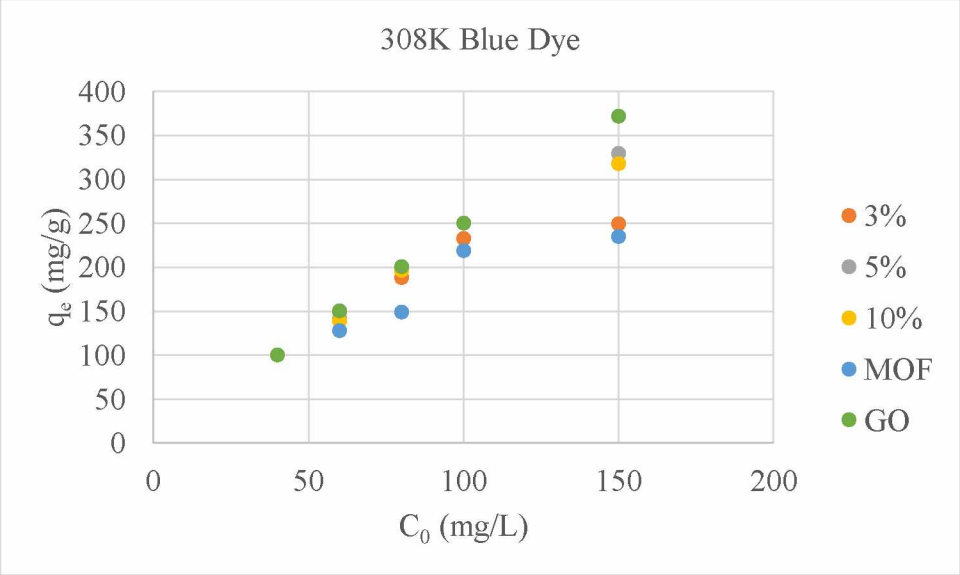
Figures 1a-f and 2a-f visually detail the previously mentioned table properties.

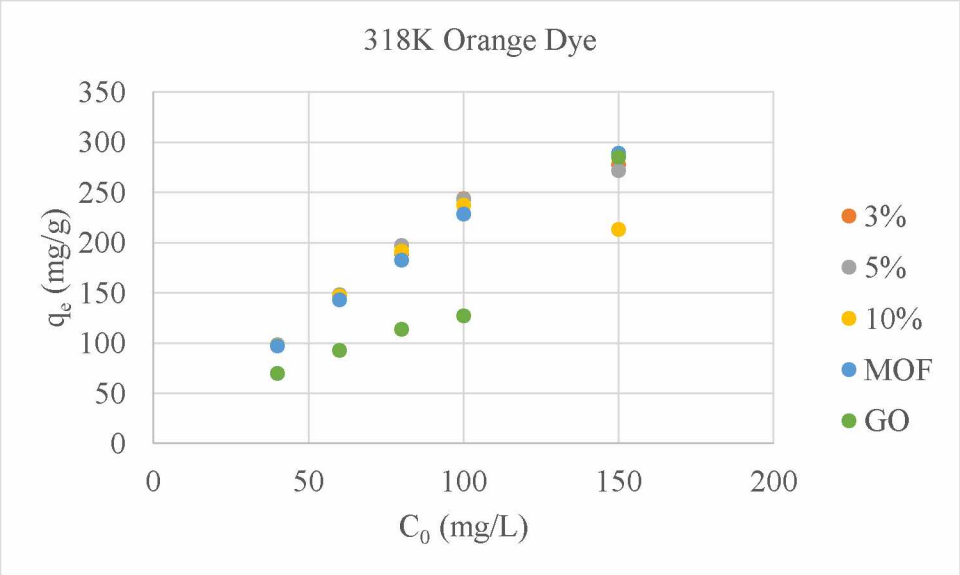
Figure 1: Adsorption of a) orange dye at 298K, b) blue dye at 298K, c) orange dye at 308K, d) blue dye at 308K, e) orange dye at 318K, and f) blue dye at 318K by various nanocomposites.






308K Orange Dye
300
250
200
150
100
50
0
q_e (mg/g)
0
50
100
150
200
C_0 (mg/L)
3%
5%
10%
MOF
GO


308K Blue Dye
400
350
300
250
200
150
100
50
0
q_e (mg/g)
0
50
100
150
200
C_0 (mg/L)
3%
5%
10%
MOF
GO


318K Orange Dye
350
300
250
200
150
100
50
0
q_e (mg/g)
0
50
100
150
200
C_0 (mg/L)
3%
5%
10%
MOF
GO

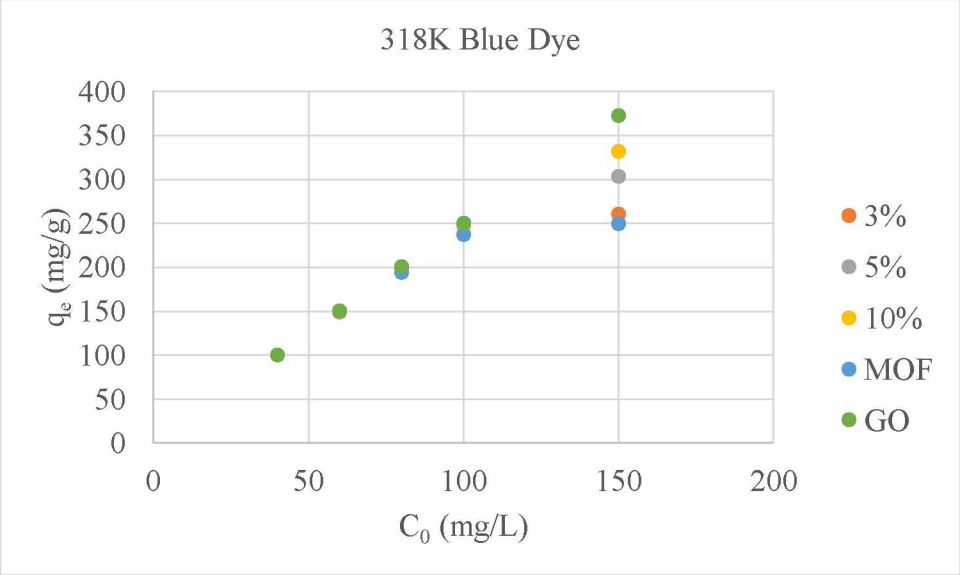
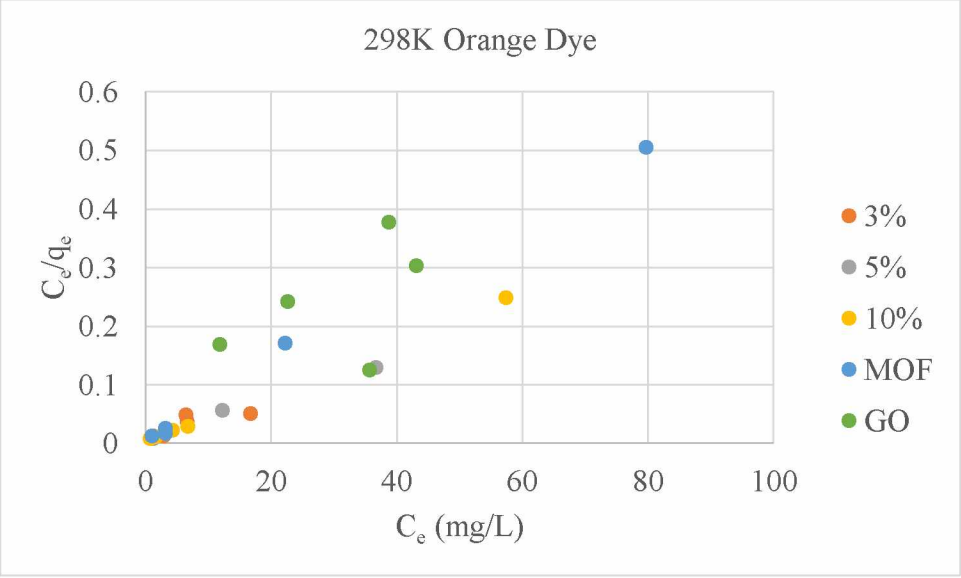
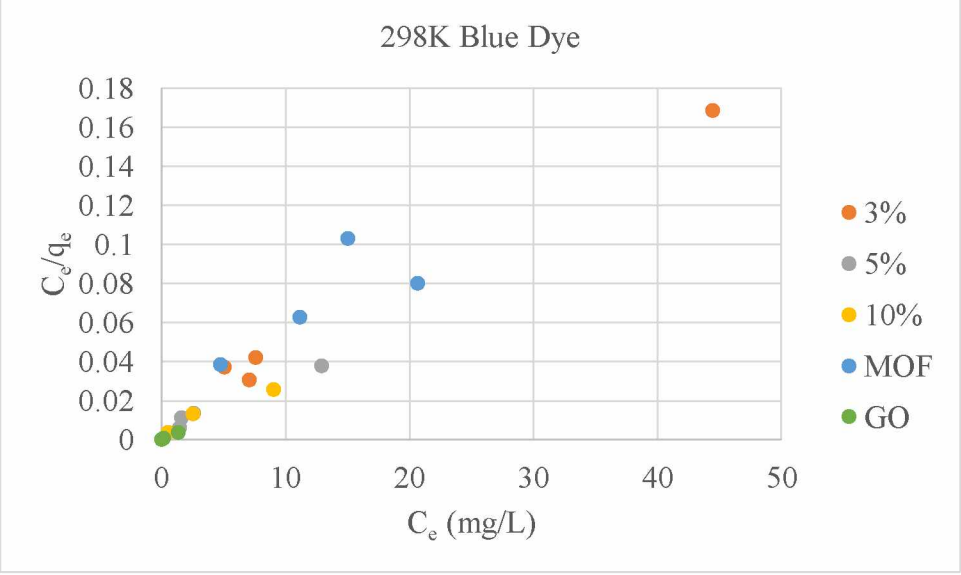
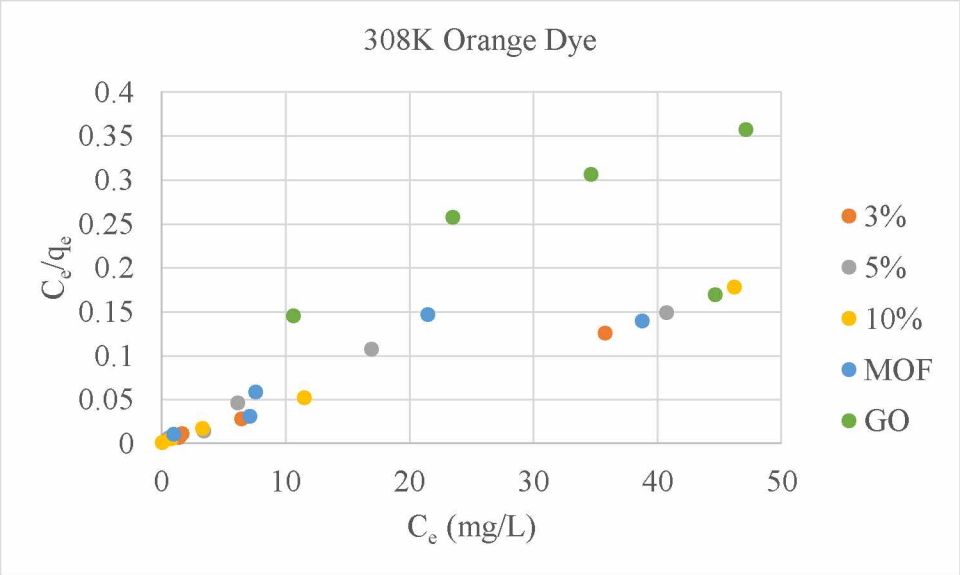
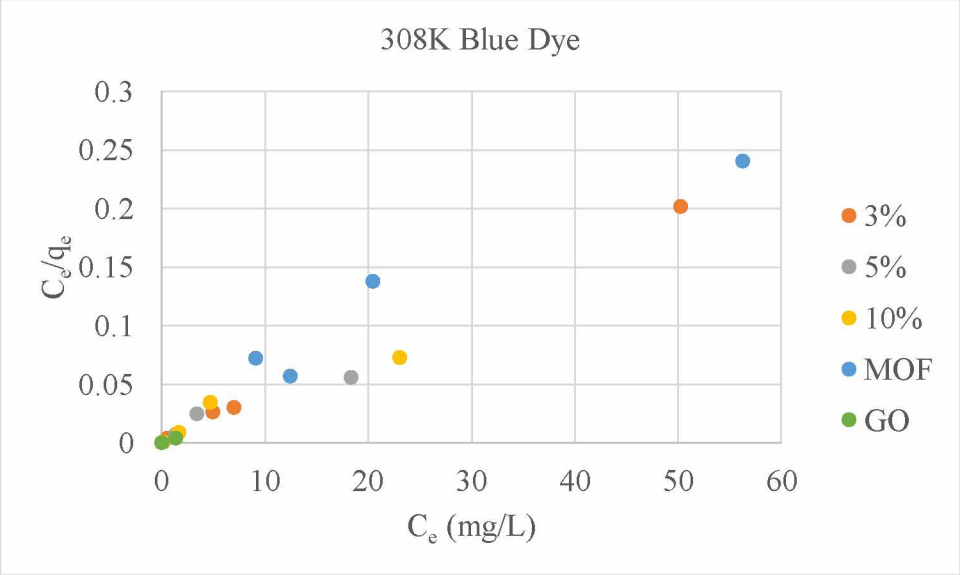

318K Blue Dye
400
350
300
250
200
150
100
50
0
q_e (mg/g)
0
50
100
150
200
C_0 (mg/L)
3%
5%
10%
MOF
GO

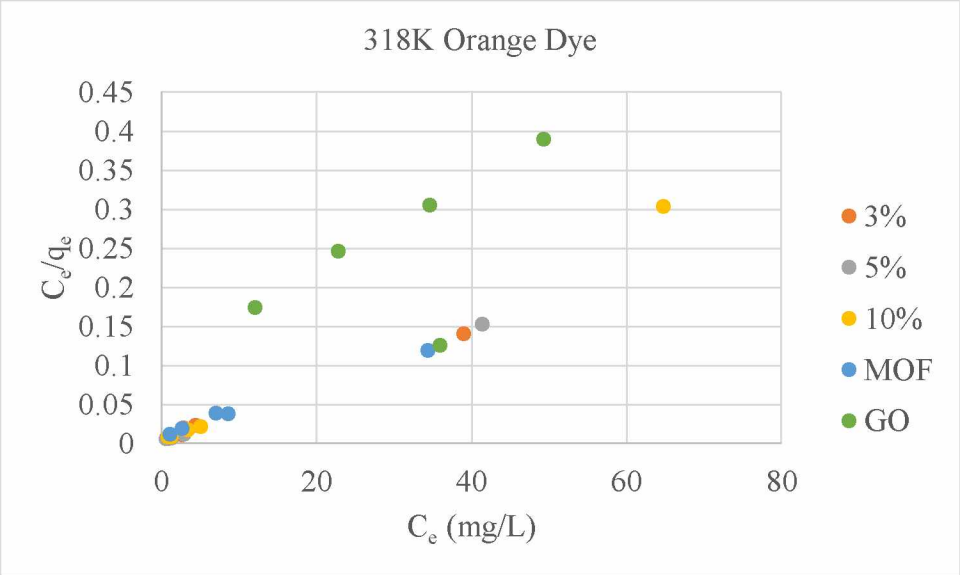
Figure 2: Langmuir isotherm models for a) orange dye at 298K, b) blue dye at 298K, c) orange dye at 308K, d) blue dye at 308K, e) orange dye at 318K, and f) blue dye at 318K of various nanocomposites.

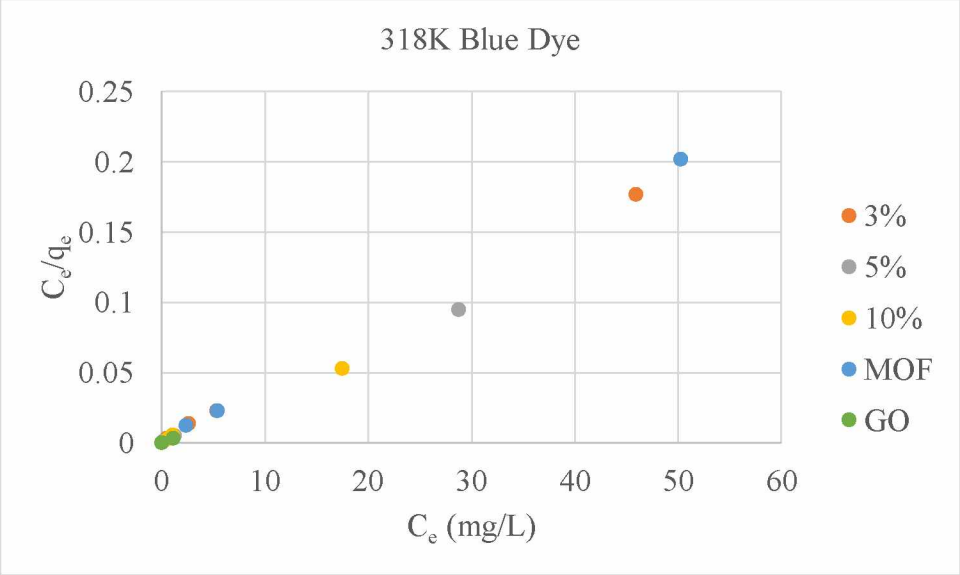





308K Orange Dye
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Ce/qe
0
10
20
30
40
50
Ce (mg/L)
3%
5%
10%
MOF
GO


308K Blue Dye
0.3
0.25
0.2
0.15
0.1
0.05
0
Ce/qe
0
10
20
30
40
50
60
Ce (mg/L)
3%
5%
10%
MOF
GO





As seen by the various tables and figures in this section, increasing operating temperature reduced data point obscurity and increased trend linearity amongst most materials. All materials at all temperatures proved to be appropriately described by the Langmuir isotherm model since all had R_L values less than one. An interesting trend amongst most composites was the Langmuir constant, K_L. Most K_Ls increased between 298K to 308K and then decreased at 318K. Maximum adsorption capacity, q_{max}, is another property effected by temperature. For most materials, apart from MIL-53 (Al), adsorption capacity decreased as temperature increased. Results also suggest that increasing operational temperature increases material's Freundlich constants and Gibbs energy change, however there appeared to be no correlation between temperature and adsorption capacity.

4. Conclusions

This project synthesized multiple MIL-53 (Al)-GO nanocomposites. Composites effectively removed dye particles from solutions of varying initial concentrations. Results showed that nanocomposites containing higher quantities of GO were better at removing blue dye particles, and materials containing less GO removed orange particles better. This is likely a result of each material's charge. GO and orange dye particles are both negatively charged, indicated by GO's lesser ability to remove orange dye. Likewise, MIL-53 (Al) and blue dye are positively charged, thus MIL-53 (Al) being less capable of absorbing blue particles. In addition, the dye adsorption capacity may be related to the surface area of the MIL-53 (Al)-GO nanocomposites, a task available for future research. It appears that composites containing more than 5% GO decreased in adsorption capacity for blue dye. This is likely due to excessive GO particles occupying the openings of the MOF, reducing the overall surface area available to enter and be trapped by the composite.

Adsorption isothermal models quantified thermodynamic responses. All materials were able to be modeled by both Freundlich and Langmuir isotherm models, but were more accurately described by Langmuir isotherm models. Increased mixing temperatures stimulated increases in Langmuir separation factors, Freundlich constants, and Gibbs free energy change. However, increased temperature appears to decrease maximum adsorption capacity. It appears that attraction forces decrease with an increase in temperature [16]. There was no correlation between adsorption capacity and temperature increase.

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